



JC10 Rec'd PCT/PTO 1 8 JAN 2002

10/031407

200 Pennsylvania Avenue, NW  
Washington, DC 20037-3213

T 202.293.7060

F 202.293.7860

www.sughrue.com

January 18, 2002

**BOX PCT**Commissioner for Patents  
Washington, D.C. 20231PCT/EP00/08057  
-filed August 17, 2000

Re: Application of Didier HAAS, Claude FUCHS, Serge FOURCAUDOT,  
Francois CHAROLLAIS and Joseph SOMERS  
METHOD FOR PRODUCING NUCLEAR FUEL PELLETS OF THE MOX  
TYPE

**Assignee: EUROPEAN COMMUNITY (EC)**

Our Ref: Q67836

Dear Sir:

The following documents and fees are submitted herewith in connection with the above application for the purpose of entering the National stage under 35 U.S.C. § 371 and in accordance with Chapter II of the Patent Cooperation Treaty:

- ☒ an executed Declaration and Power of Attorney.
- ☒ a copy of the International Publication
- ☒ Notification Concerning Submission or Transmittal of Priority Document.
- ☒ an executed Assignment and PTO 1595 form.
- ☒ International Search Report, Information Disclosure Statement and a Form PTO-

1449.

It is assumed that copies of the International Application, the International Search Report, the International Preliminary Examination Report, and any Articles 19 and 34 amendments as required by § 371(c) will be supplied directly by the International Bureau, but if further copies are needed, the undersigned can easily provide them upon request.

Applicant claims benefit of small entity status in accordance with 37 CFR § 1.27.

The Government filing fee is calculated as follows (**Small Entity fees apply**):

Total claims	12	-	20	=		x	\$9.00	=	\$0.00
Independent claims	1	-	3	=		x	\$42.00	=	\$0.00
Base Fee									\$445.00
Multiple Dependent Claim Fee									\$140.00

**TOTAL FILING FEE**

\$585.00

**Recordation of Assignment**

\$ 40.00

**TOTAL FEE**

\$625.00



Sughrue

SUGHRUE MION, PLLC

10/031407  
JSTB Rec'd PCT/PTO 18 JAN 2002

Checks for the statutory filing fee of \$585.00 and Assignment recordation fee of \$40.00 are attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. §§ 1.16, 1.17 and 1.492 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Priority is claimed from:

Country

European

Application No

99116886.5

Filing Date

September 6, 1999

Respectfully submitted,

Sheldon I. Landsman

Sheldon I. Landsman

Registration No. 25,430

SIL/amt

10031407 01 JAN 2002

METHOD FOR PRODUCING NUCLEAR FUEL PELLETS OF THE MOX TYPE

This invention refers to a method for producing nuclear fuel pellets of the MOX (= mixed oxide) type, comprising the steps of

- preparing an U-Pu oxide blend powder having a Pu content in excess of the finally desired value,
- preparing an uranium oxide powder,
- mixing adequate quantities of both powders in order to achieve the desired plutonium content,
- compacting and sintering the mixture for obtaining said pellets.

Such a method is known under the term MIMAS ("Micronized MASTER Blend" - see for example D. Haas, M. Lippens "MOX FUEL FABRICATION AND IN-REACTOR PERFORMANCE", Proc. of the Internat. Conference on Future Nuclear Systems, GLOBAL 97, p.489 à 494). This separate preparation of a powder free of plutonium reduces the volume of plutonium containing powder that has to be milled, and allows the production of fuel pellets of various plutonium contents with a unique plutonium treatment chain by changing only the rate of admixed uranium powder.

The commercial powders currently used, however, result in a final product which is heterogeneous, i.e. contains large particles rich in plutonium oxide dispersed within an uranium oxide matrix whose grain size is below 10  $\mu\text{m}$ . This heterogeneity leads to two major drawbacks:

During irradiation localised higher fissile material concentrations lead to high local burnups, to fission damages and to gas release. To limit this gas release large  $\text{UO}_2$  grains are recommended, provided that they are produced without additives that might lead to detrimental fuel behaviour during irradiation and might also lead to difficulties during reprocessing.

During reprocessing the dissolution of the burned-up fuel in nitric acid is hindered by regions rich in pluto-

nium, which is notoriously insoluble.

The present invention aims to overcome these drawbacks and to propose a method as indicated above which leads to fuel pellets of the MOX type in which the distribution of plutonium throughout the pellet is substantially more homogeneous.

This aim is achieved by the method as defined in claim 1. As far as preferred embodiments of this method are concerned, reference is made to the secondary claims.

The invention will now be described in detail by means of preferred embodiments.

In agreement with the known MIMAS method as cited above, the method according to the invention implies the separate preparation of a Pu-U oxide powder on the one hand and an uranium oxide powder free of plutonium on the other hand.

According to a first embodiment the Pu-U oxide powder is prepared conventionally by mechanically milling  $\text{PuO}_2$  and  $\text{UO}_2$  materials, whereas the  $\text{UO}_2$  powder is prepared as follows:

To an aqueous solution of uranyl nitrate small amounts, i.e. between 0.5 and 2 wt%, of organic thickeners are added, such as methocel, dextran, polyvinyl alcohol, such that the viscosity of the solution is adjusted to values between 20 and 100 centipoise. There-after, this solution is dispersed into droplets, which are introduced into an ammonia bath. In this bath, due to the network formed by the long chain organic polymers, precipitation occurs within the original droplets, so that nearly spherical beads are formed. The size of these beads depends on the size of the droplets produced during dispersion. In a preferred embodiment these beads present diameters of between 20 and 50  $\mu\text{m}$ . These beads are then washed to remove nitrate salts (ammonium nitrate salts in the above example) and organic polymers, and are subjected to an azeotropic distillation using an immiscible organic solvent such as  $\text{C}_2\text{Cl}_4$  to

remove water.

Once dried the beads are in a hydroxide form, from which they are converted to oxide by a thermal treatment of between 2 and 6 hours duration and at about 400°C in air.

5 Thereby residual organic polymers are pyrolysed. The beads are then again submitted to a thermal treatment of between 4 and 8 hours duration, this time at about 800°C and in a reducing atmosphere of Ar/5% $H_2$ , to convert  $U_3O_8$  to  $UO_2$ .

10 The beads can be produced by conventional uranium processing facilities (no  $\alpha$  contamination). They are free flowing, dust free and do not require any further mechanical treatment such as milling prior to mixing with the powder containing plutonium. The homogeneity of the finally produced fuel can further be enhanced by sieving the beads and retaining only beads with diameters in the range of 20 to 50 $\mu$ m. Alternatively this result can also be achieved by using a droplet dispersion device which produces droplets of well defined size such that the bead diameters remain within said range and no sieving becomes necessary.

20 Once mixed the MOX powder is compacted into pellets by using a press which applies a pressure of between 200 and 600 MPa. These pellets are then sintered at high temperature, preferably at 1700°C, in a humidified Ar/ $H_2$  atmosphere, the hydrogen content of which lies between 1 and 6% and the water vapour introduction should result in a ratio of the partial  $H_2$  pressure to the water vapour partial pressure of between 20 and 60. The water allows to control the oxygen potential of the gas atmosphere which results in an enhanced diffusion and in a more homogeneous fuel thus enabling a longer burn-up in the reactor.

30 According to a variant of the method the powder containing an excess content of plutonium can be prepared in the same way as above described for the uranium oxide powder, but by starting with uranyl-plutonium nitrate instead of uranyl nitrate.

35

- 4 -

The inventive method can be realised in conventional MOX fabrication facilities and conserves all the advantages of the MIMAS process but does not suffer from the drawbacks of this process as mentioned above.

10034407 011802

CLAIMS

5           1. A method for producing nuclear fuel pellets of the MOX (mixed plutonium and uranium oxide) type, comprising the steps of

- preparing an U-Pu oxide blend powder having a Pu content in excess of the finally desired value,
- 10       - preparing an uranium oxide powder,
- mixing adequate quantities of both powders in order to achieve the desired plutonium content,
- compacting and sintering the mixture for obtaining said pellets,

15       characterized in that the step of preparing the uranium oxide powder involves the following sequence of substeps:

a) preparation of an aqueous solution of uranyl nitrate to which between 0.5 and 2 wt% of organic thickeners are added such that the viscosity of the solution is adjusted to  
20       values between 20 and 100 centipoise,

- b) dispersion of the solution into droplets,
- c) introducing said droplets into a hydroxide bath,
- d) washing the resulting beads,
- e) drying the beads by azeotropic distillation using an  
25       immiscible organic solvent,

f) thermal treatment of the beads in an oxidising atmosphere,

g) thermal treatment in a reducing atmosphere.

30           2. A method according to claim 1, characterized in that the step of preparing an U-Pu oxide blend powder consists in milling and mixing adequate quantities of uranium oxide and plutonium oxide.

35           3. A method according to claim 1, characterized in

that the step of preparing the U-Pu oxide blend powder involves the following sequence of substeps:

- a) preparation of an aqueous solution of uranyl-plutonium nitrate to which small amounts of organic thickeners are added in order to adjust the viscosity of the solution to values between 20 and 100 centipoise,
- b) dispersion of the solution into droplets,
- c) introducing said droplets into a hydroxide bath,
- d) washing the resulting beads,
- e) subjecting the beads to an azeotropic distillation using an immiscible organic solvent,
- f) thermal treatment of the beads in an oxidising atmosphere,
- g) thermal treatment in a reducing atmosphere.

4. A method according to anyone of the preceding claims, characterized in that in substep a) the organic thickeners are selected among methocel, dextran and polyvinyl alcohol.

5. A method according to anyone of the preceding claims, characterized in that in substep c) the hydroxide bath consists of ammonia.

6. A method according to anyone of the preceding claims, characterized in that in substep f) the thermal treatment in an oxidising atmosphere is performed at about 400°C and in air.

7. A method according to anyone of the preceding claims, characterized in that in substep g) the thermal treatment in a reducing atmosphere is performed at about 800°C, the reducing atmosphere containing an inert gas with a hydrogen content between 1 and 6%.



8. A method according to anyone of the preceding claims, characterized in that compacting of the powder mixture into pellets is obtained by applying a pressure of between 200 and 600 MPa.

5

9. A method according to anyone of the preceding claims, characterized in that the sintering of the pellets takes place at a temperature above 1200°C, preferably between 1600 and 1700°C, and in a humidified Ar/H<sub>2</sub> atmosphere, the hydrogen content lying between 1% and 6% and the ratio between the partial pressures of hydrogen and water vapour being selected between 20 and 60.

10. A method according to anyone of the preceding claims, characterized in that before mixing adequate quantities of both powders, the  $\text{UO}_2$ -powder is sieved in order to retain only beads with diameters between 20 and 50 $\mu\text{m}$  size.

1870 1871 1872 1873 1874 1875 1876 1877 1878 1879 1880 1881 1882 1883 1884 1885 1886 1887 1888 1889 1890 1891 1892 1893 1894 1895 1896 1897 1898 1899 1900 1901 1902 1903 1904 1905 1906 1907 1908 1909 1910 1911 1912 1913 1914 1915 1916 1917 1918 1919 1920 1921 1922 1923 1924 1925 1926 1927 1928 1929 1930 1931 1932 1933 1934 1935 1936 1937 1938 1939 1940 1941 1942 1943 1944 1945 1946 1947 1948 1949 1950 1951 1952 1953 1954 1955 1956 1957 1958 1959 1960 1961 1962 1963 1964 1965 1966 1967 1968 1969 1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1981 1982 1983 1984 1985 1986 1987 1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023 2024 2025 2026 2027 2028 2029 2030 2031 2032 2033 2034 2035 2036 2037 2038 2039 2040 2041 2042 2043 2044 2045 2046 2047 2048 2049 2050 2051 2052 2053 2054 2055 2056 2057 2058 2059 2060 2061 2062 2063 2064 2065 2066 2067 2068 2069 2070 2071 2072 2073 2074 2075 2076 2077 2078 2079 2080 2081 2082 2083 2084 2085 2086 2087 2088 2089 2090 2091 2092 2093 2094 2095 2096 2097 2098 2099 2100 2101 2102 2103 2104 2105 2106 2107 2108 2109 2110 2111 2112 2113 2114 2115 2116 2117 2118 2119 2120 2121 2122 2123 2124 2125 2126 2127 2128 2129 2130 2131 2132 2133 2134 2135 2136 2137 2138 2139 2140 2141 2142 2143 2144 2145 2146 2147 2148 2149 2150 2151 2152 2153 2154 2155 2156 2157 2158 2159 2160 2161 2162 2163 2164 2165 2166 2167 2168 2169 2170 2171 2172 2173 2174 2175 2176 2177 2178 2179 2180 2181 2182 2183 2184 2185 2186 2187 2188 2189 2190 2191 2192 2193 2194 2195 2196 2197 2198 2199 2200 2201 2202 2203 2204 2205 2206 2207 2208 2209 2210 2211 2212 2213 2214 2215 2216 2217 2218 2219 2220 2221 2222 2223 2224 2225 2226 2227 2228 2229 2230 2231 2232 2233 2234 2235 2236 2237 2238 2239 2240 2241 2242 2243 2244 2245 2246 2247 2248 2249 2250 2251 2252 2253 2254 2255 2256 2257 2258 2259 2260 2261 2262 2263 2264 2265 2266 2267 2268 2269 2270 2271 2272 2273 2274 2275 2276 2277 2278 2279 2280 2281 2282 2283 2284 2285 2286 2287 2288 2289 2290 2291 2292 2293 2294 2295 2296 2297 2298 2299 2300 2301 2302 2303 2304 2305 2306 2307 2308 2309 2310 2311 2312 2313 2314 2315 2316 2317 2318 2319 2320 2321 2322 2323 2324 2325 2326 2327 2328 2329 2330 2331 2332 2333 2334 2335 2336 2337 2338 2339 2340 2341 2342 2343 2344 2345 2346 2347 2348 2349 2350 2351 2352 2353 2354 2355 2356 2357 2358 2359 2360 2361 2362 2363 2364 2365 2366 2367 2368 2369 2370 2371 2372 2373 2374 2375 2376 2377 2378 2379 2380 2381 2382 2383 2384 2385 2386 2387 2388 2389 2390 2391 2392 2393 2394 2395 2396 2397 2398 2399 2400 2401 2402 2403 2404 2405 2406 2407 2408 2409 2410 2411 2412 2413 2414 2415 2416 2417 2418 2419 2420 2421 2422 2423 2424 2425 2426 2427 2428 2429 2430 2431 2432 2433 2434 2435 2436 2437 2438 2439 2440 2441 2442 2443 2444 2445 2446 2447 2448 2449 2450 2451 2452 2453 2454 2455 2456 2457 2458 2459 2460 2461 2462 2463 2464 2465 2466 2467 2468 2469 2470 2471 2472 2473 2474 2475 2476 2477 2478 2479 2480 2481 2482 2483 2484 2485 2486 2487 2488 2489 2490 2491 2492 2493 2494 2495 2496 2497 2498 2499 2500 2501 2502 2503 2504 2505 2506 2507 2508 2509 2510 2511 2512 2513 2514 2515 2516 2517 2518 2519 2520 2521 2522 2523 2524 2525 2526 2527 2528 2529 2530 2531 2532 2533 2534 2535 2536 2537 2538 2539 2540 2541 2542 2543 2544 2545 2546 2547 2548 2549 2550 2551 2552 2553 2554 2555 2556 2557 2558 2559 2560 2561 2562 2563 2564 2565 2566 2567 2568 2569 2570 2571 2572 2573 2574 2575 2576 2577 2578 2579 2580 2581 2582 2583 2584 2585 2586 2587 2588 2589 2590 2591 2592 2593 2594 2595 2596 2597 2598 2599 2600 2601 2602 2603 2604 2605 2606 2607 2608 2609 2610 2611 2612 2613 2614 2615 2616 2617 2618 2619 2620 2621 2622 2623 2624 2625 2626 2627 2628 2629 2630 2631 2632 2633 2634 2635 2636 2637 2638 2639 2640 2641 2642 2643 2644 2645 2646 2647 2648 2649 2650 2651 2652 2653 2654 2655 2656 2657 2658 2659 2660 2661 2662 2663 2664 2665 2666 2667 2668 2669 2670 2671 2672 2673 2674 2675 2676 2677 2678 2679 2680 2681 2682 2683 2684 2685 2686 2687 2688

**DECLARATION AND POWER OF ATTORNEY**

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name: that I verily believe I am the original, first and sole inventor (if only one name is listed below) or a joint inventor (if plural names are listed below) of the subject matter claimed and for which a patent is sought in the application entitled:

which application is:

the attached application  
(for original application)

**PCT** application Serial No. **PCT/EP00/08057**  
filed **Aug. 17, 2000**, and amended on

(for declaration not accompanying application)

that I have reviewed and understand the contents of the specification of the above-identified application, including the claims, as amended by any amendment referred to above; that I acknowledge my duty to disclose information of which I am aware which is material to the patentability of this application under 37 C.F.R. 1.56, that I hereby claim foreign priority benefits under Title 35, United States Code §119, §172 or §365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified on said list any foreign application for patent or inventor's certificate on this invention having a filing date before that of the application on which priority is claimed:

Application Number	Country	Filing Date	Priority Claimed (yes or no)
<b>92116886.5</b>	<b>Europe</b>	<b>Sept. 6, 1999</b>	<b>yes</b>

I hereby claim the benefit of Title 35, United States Code §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in a listed prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge my duty to disclose any information material to the patentability of this application under 37 C.F.R. 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Application Serial No.	Filing Date	Status (patented, pending, abandoned)
<p>I hereby appoint John H. Mion, Reg. No. <u>18,879</u>; Donald E. Zinn, Reg. No. <u>19,046</u>; Thomas J. Macpeak, Reg. No. <u>19,292</u>; Robert J. Seas, Jr., Reg. No. <u>21,092</u>; Darryl Mexic, Reg. No. <u>23,063</u>; Robert V. Sloan, Reg. No. <u>22,775</u>; Peter D. Olexy, Reg. No. <u>24,513</u>; J. Frank Osha, Reg. No. <u>24,625</u>; Waddell A. Biggart, Reg. No. <u>24,861</u>; Robert G. McMorrow, Reg. No. <u>19,093</u>; Louis Gubinsky, Reg. No. <u>24,835</u>; Neil B. Siegel, Reg. No. <u>25,200</u>; David J. Cushing, Reg. No. <u>28,703</u>; John R. Inge, Reg. No. <u>26,916</u>; Joseph J. Ruch, Jr., Reg. No. <u>26,577</u>; Sheldon I. Landsman, Reg. No. <u>25,430</u>; Richard C. Turner, Reg. No. <u>29,710</u>; Howard L. Bernstein, Reg. No. <u>25,665</u>; Alan J. Kasper, Reg. No. <u>25,426</u>; Kenneth J. Burchfiel, Reg. No. <u>31,333</u>; Gordon Kit, Reg. No. <u>30,764</u>; Susan J. Mack, Reg. No. <u>30,951</u>; Frank L. Bernstein, Reg. No. <u>31,484</u>; Mark Boland, Reg. No. <u>32,197</u>; William H. Mandir, Reg. No. <u>32,156</u>; Scott M. Daniels, Reg. No. <u>32,562</u>; Brian W. Hannon, Reg. No. <u>32,778</u> and Abraham J. Rosner, Reg. No. <u>33,276</u>, my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, and request that all correspondence about the application be addressed to <b><u>SUGHRUE, MION, ZINN, MACPEAK &amp; SEAS</u></b>, 2100 Pennsylvania Avenue, N.W., Washington, D.C. 20037-3202.</p>		

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date 05/05/00

First Inventor Didier HAAS  
First Name Middle Initial Last Name

Residence Eisbergweg 12  
76356 Weingarten

Signature [Signature]

Post Office Address Eisbergweg 12

Citizenship Belgium

D-76356 Weingarten/Germany **DEX**

2-0 Date 05. Mai 2000 Second Inventor Claude FUCHS  
First Name Middle Initial Last Name  
Residence Niederlauterbach/France <sup>FRX</sup> Signature [Signature]  
Post Office Address 4, Place de la Chapelle  
Citizenship France F-67360 NIEDERLAUTERBACH

3-0 Date 05. Mai 2000 Third Inventor Serge FOURCAUDOT  
First Name Middle Initial Last Name  
Residence Karlsruhe/Germany <sup>DEX</sup> Signature [Signature]  
Post Office Address Karlsstr. 99  
Citizenship French D-76137 KARLSRUHE

4-0 Date 05. Mai 2000 Fourth Inventor François CHAROLLAIS  
First Name Middle Initial Last Name  
Residence Linkenheim/Germany <sup>DEX</sup> Signature [Signature]  
Post Office Address Bahnhofstr. 16b  
Citizenship French D-76351 LINKENHEIM

5-0 Date 05. Mai 2000 Fifth Inventor Joseph SOMERS  
First Name Middle Initial Last Name  
Residence Karlsruhe/Germany <sup>DEX</sup> Signature [Signature]  
Post Office Address Reinhold-Frank-Str. 4  
Citizenship Irish D-76133 KARLSRUHE

Date \_\_\_\_\_ Sixth Inventor \_\_\_\_\_  
First Name Middle Initial Last Name  
Residence \_\_\_\_\_ Signature \_\_\_\_\_  
Post Office Address \_\_\_\_\_  
Citizenship \_\_\_\_\_

Date \_\_\_\_\_ Seventh Inventor \_\_\_\_\_  
First Name Middle Initial Last Name  
Residence \_\_\_\_\_ Signature \_\_\_\_\_  
Post Office Address \_\_\_\_\_  
Citizenship \_\_\_\_\_